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Photocatalytic removal of Cr(VI) and Ni(II) by UV/TiO_2: kinetic study

Mehdi Shirzad Siboni[a], Mohammad-Taghi Samadi[b], Jae-Kyu Yang[c], Seung-Mok Lee[d,]*

[a]*Environmental Health Research Centre, Kurdistan University of Medical Sciences, Kurdistan Sanandaj, Iran*
[b]*Department of Environmental Health, Hamadan University of Medical Science, Hamadan, Kurdistan Sanandaj, Iran*
[c]*Division of General Education, Kwangwoon University, Seoul, Korea*
[d]*Department of Environmental Engineering, Kwandong University, Gangnung, Korea*
Tel. +82 33 649 7535; Fax: +82 33 642 7635; email: leesm@kd.ac.kr

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ABSTRACT

In this study, photocatalytic removal of Cr(VI) and Ni(II) by illuminated TiO_2 was investigated with variation of solution pH, contact time, TiO_2 dosage and initial Cr(VI) and Ni(II) concentration. From the photocatalytic reaction, near complete elimination of Cr(VI) and Ni(II) occurred from the adsorption of Cr(VI) and Ni(II) on the surface of TiO_2 as well as reduction of Cr(VI) and Ni(II) to Cr(III) and Ni(0), respectively. Reduction was recognized as a significant elimination process for the treatment Cr(VI) and Ni(II) from wastewater. Removal of Cr(VI) decreased with increasing pH while removal of Ni(II) increased with increasing pH. TiO_2 dosage was also an important parameter for the removal of Cr(VI). As the TiO_2 dosage increased up to 1 g l^{-1}, removal of Cr(VI) and Ni(II) was continuously enhanced.

Keywords: Cr(VI); Ni(II); TiO_2; Photocatalytic reduction; Adsorption; Kinetic

1. Introduction

Rapid industrialization and urbanization have been contaminating the existing water resources by organics and heavy metals. The presence of heavy metals in the aquatic environment is a serious concern in the living organisms because of their toxicity [1,2]. Heavy metal ions such as Cr(VI) and Ni(II) are assimilated, stored, and concentrated by organisms those are exposed to low concentrations of these substances for long periods or repeatedly exposed to high concentrations of them for short periods [2–5]. The fate of chromium and nickel in the environment is closely linked to its chemistry. In aquatic environments, chromium presents as Cr(VI) and Cr(III). And nickel presents as Ni(II) and Ni^0 [2,3,6,7]. Cr(VI) and Ni(II) is extremely toxic to human while Cr(III) and Ni^0 is only slightly toxic. In addition, removal of Cr(III) and Ni^0 through adsorption on solid phase is not an efficient method compared to Cr(VI) and Ni(II) [8,9]. The safe and effective treatment of wastewater containing heavy metals is always a challenging task due to a fact that cost-effective treatment methods are not much available. Ion exchange, direct precipitation and adsorption are the widely used methods in the removal of dissolved heavy metals. These methods require large surface area exposed to liquid and long detention periods. Moreover most of these methods need high capital cost and recurring expenses such as chemicals, which are not suitable for small-scale industries [10–13].

To overcome these problems, advanced oxidation processes (AOP) have been widely studied and are recommended as a talented technique [14–16].

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*Corresponding author.

Overall, AOPs use hydroxyl free radical (•OH), as a strong oxidant, in order to destroy organic compounds that cannot be oxidized by conventional oxidants such as oxygen, ozone and chlorine [8,9,17–21]. The other methods used to generate hydroxyl radicals in aqueous solutions are O_3/UV, H_2O_2/UV, Fe(II)/H_2O_2 and TiO_2/UV [22–24]. Among these methods, photocatalytic reaction using TiO_2/UV can treat organic compounds and heavy metals at the same time. Photocatalytic reduction of Cr(VI) has been widely investigated in the presence of organic compounds such as dye, oxalate, humic acid [25–27]. Most of these studies reported that reduction of Cr(VI) proceeded quickly in the presence of organic compounds than that observed in the Cr(VI) alone. In addition, this technique can transform non-biodegradable organic compounds to biodegradable organic residues. Therefore this technique can be used as pre- or post-treatment methods in the traditional wastewater treatment process because of its easiness in installation and operation [14,27–29]. However there is very limited information for the photocatalytic reduction of both cationic and anionic heavy metal ions contaminated in the water at the same time.

The present study investigated elimination efficiencies of Cr(VI) in the presence of Ni(II) and vice versa by TiO_2/UV photocatalysis with variation of the solution pH, contact time, TiO_2 dosage and initial Cr(VI) and Ni(II) concentration. In addition, kinetic parameters were obtained by application of first-order equation.

2. Materials and methods

2.1. Materials

Degussa P-25 TiO_2 (80% anatase and 20% rutile) obtained from Aeroxide was used as a photocatalyst in this work. It has approximately spherical shape and nonporous property with purity greater than 99.5%. The specific surface area (BET) of the TiO_2 particles was 50 ± 15 $m^2\ g^{-1}$ (Evonik-Industrial Co), and average particle size of the TiO_2 powder was 21 nm.

2.2. Experimental setup

The experimental setup for photocatalytic reduction of Cr(VI) and Ni(II) by UV/TiO_2 is schematically shown in Fig. 1. A 125 W medium-pressure UV-lamp emitting maximum wavelength at 247.3 nm and light intensity equal to 1020 $\mu W\ cm^{-2}$ (according to Shokofan Tosee company in Iran) was used as the radiation source. The reactor consists of two compartments: the outer one can be contained 2 l solution and a UV lamp is placed in the inner one. The outer part of the reactor is a 10 l water-bath maintained at 25°C for all experiments. All photocatalytic experiments were performed in a 1000 ml reactor. During the experiment, the test solution in the reactor was constantly stirred using a rotary mixer (H1-190M; Hanna Instruments, Kehl am Rhein, Germany).

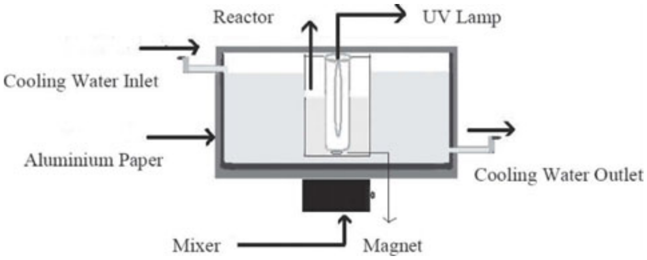
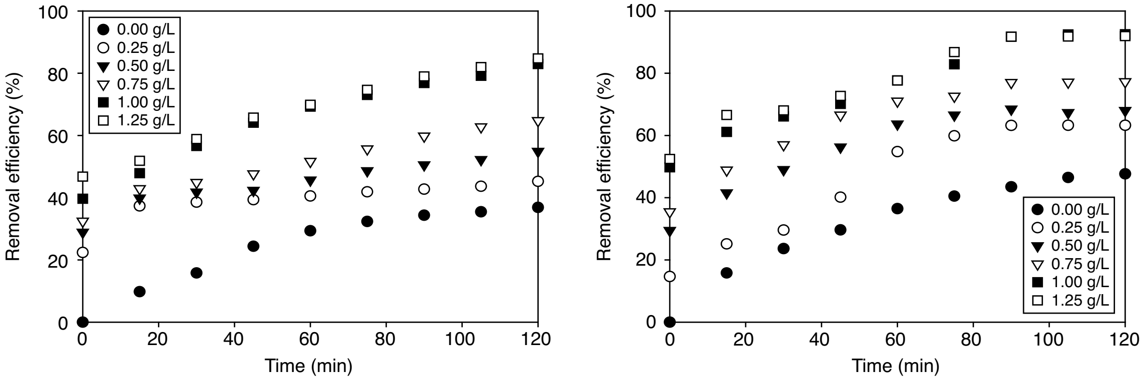


Fig. 1. The schematic diagram of the experimental set-up for photocatalysis of Ni(II) and Cr(VI).

2.3. Photocatalytic experiments

Stock solution (1000 mg l^{-1}) of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Merck, Germany) into deionized water. The Ni(II) stock solution (100 mg l^{-1}) was prepared by the following method. The 0.1 g nickel metal (Merck, Germany) was dissolved in 10 ml conc-HNO_3 (Merck, Germany) solution at 60–70°C then it was diluted with deionized water. Experimental solutions of the desired concentrations were obtained by successive dilutions. In batch tests, a selected dosage of TiO_2 (0, 0.25, 0.5, 0.75, 1, 1.25 g l^{-1}) was introduced into 1000-ml Cr(VI) and Ni(II) solution of a known concentration (5, 15, 20 mg l^{-1}) adjusted at pH 3, 7 and 11. The initial solution pH was adjusted by adding 0.1 M NaOH and HCl (Merck, Germany). And continuous pH adjustment was performed with 0.1 M HCl or NaOH during photocatalytic reaction in order to maintain the initial solution pH. All experiments were performed under ambient conditions for 2 h. TiO_2 suspensions with Cr(VI) and Ni(II) were equilibrated in the dark for 30 min. After the equilibration period, the UV-lamp was turned on and the solution was periodically collected from the reactor. At each selected time intervals, 10 ml solution was taken from the suspension. All the samples were covered by aluminum foil to avoid sunlight. All experiments were accomplished at 25 ± 2°C. The aqueous samples were centrifuged (Sigma-301; Sigma-Aldrich, Osterrode am Harz, Germany) at 4000 rpm for 60 min to remove TiO_2 particles and then dissolved Cr(VI) and Ni(II) was analyzed. Cr(VI) was analyzed by 1,5-diphenylcarbazide method by a spectrophotometer (HACH-DR 2500; HACH Co., Loveland, CO, USA) at a wavelength of 540 nm. Ni(II) concentration in the solution was measured by Flame Atomic Absorption Spectrometry (AA, Thermo Jarrell Ash, Smith Hieftje 22, Japan) [30].



(a) Cr(VI)

(b) Ni(II)

Fig. 2. Effect of TiO_2 dosage on the removal of (a) Cr(VI) and (b) Ni(II) (pH = 7, [Cr(VI)] and [Ni(II)] = 15 mg l^{-1}).

3. Results and discussion

3.1. Effect of TiO_2 dosage and contact time on the removal of Cr(VI) and Ni(II)

Removal of Cr(VI) and Ni(II) was investigated by varying the initial TiO_2 dosage (0, 0.25, 0.5, 0.75, 1.0, 1.25 g l^{-1}) at initial pH 7 and at constant Cr(VI) and Ni(II) concentration (15 mg l^{-1}) up to 120 min. In addition, effect of contact time on the reduction of Cr(VI) and Ni(II) was investigated by varying the contact time (15–120 min) at initial pH 7 and at constant Cr(VI) and Ni(II) concentration (15 mg l^{-1}) and TiO_2 dosage (1 g l^{-1}). Fig. 2a and b show the effect of TiO_2 dosage and contact time on the removal of Cr(VI) and Ni(II), respectively. At the initial reaction time (t = 0) before photocatalytic reaction, the percent removal of both Cr(VI) and Ni(II) increased as the TiO_2 dosage increased. This trend can be explained by favorable adsorption of both Cr(VI) and Ni(II) by increased adsorption sites. As shown in Fig. 2a, the reduced amount of Cr(VI) by UV-alone system was approximately 33% after 2 h. This amount was much higher than the previous results reported by Yang and Lee [27]. The gradually increased nickel removal by UV-alone system as shown in Fig. 2b can be explained by the precipitation of Ni^{2+} in solution. With increasing TiO_2 dosage from 0.25 to 1.25 g l^{-1} and contact time up to 120 min, the removal efficiency of Cr(VI) and Ni(II) increased because of the increased adsorption sites on the TiO_2 as well as the increased photocatalytic reduction of Cr(VI) by more free electrons generated in the conduction band [31].

In order to evaluate effect of TiO_2 dosage on the removal rate of Cr(VI) and Ni(II), a simplified first-order rate equation was applied (Eq. (1)):

$$\ln\left[C_0 / C\right] = k_1 t \qquad (1)$$

where C_0 and C is the Cr(VI) and Ni(II) concentration at initial time (t = 0) and time t; respectively; k_1 is the first-order rate constant and t is the reaction time. Fig. 3 shows the correlation between TiO_2 dosage and the first-order rate constant of Cr(VI) and Ni(II). The first-order rate constants of Cr(VI) and Ni(II) increased as the TiO_2 dosage increased up to 1 g l^{-1}. Based on this trend, an optimum TiO_2 dosage was determined as 1 g l^{-1}.

3.2. Effect of pH on the removal of Cr(VI) and Ni(II)

From the blank test with TiO_2 alone, adsorption was an important process for the removal of Cr(VI) and Ni(II) depending on the solution pH (data not shown). This result was well matched with the initial removal data of Cr(VI) and Ni(II) during the photocatalysis with UV/TiO_2 as shown in Fig. 4a and b. Under illumination by the UV lamp, the Cr(VI) solution gradually lost its originally yellow color while the white TiO_2 turned into pale green. The product of photocatalytic reduction of Cr(VI) with illuminated TiO_2 might be Cr(III). While the product of photocatalytic reduction of Ni(II) with illuminated TiO_2 might be Ni(0).

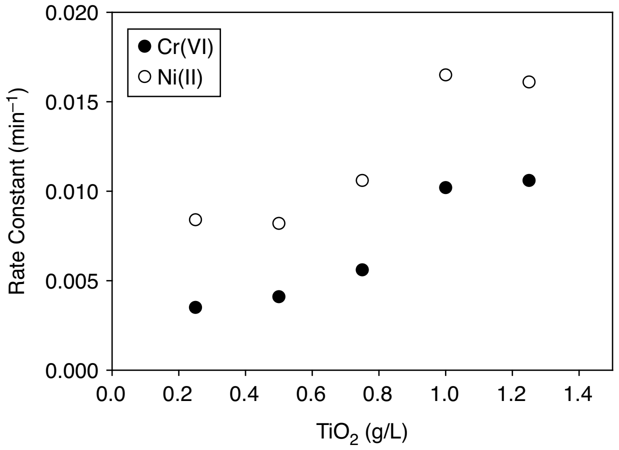


Fig. 3. Correlation between TiO_2 dosage and the first-order rate constant of Cr(VI) and Ni(II).

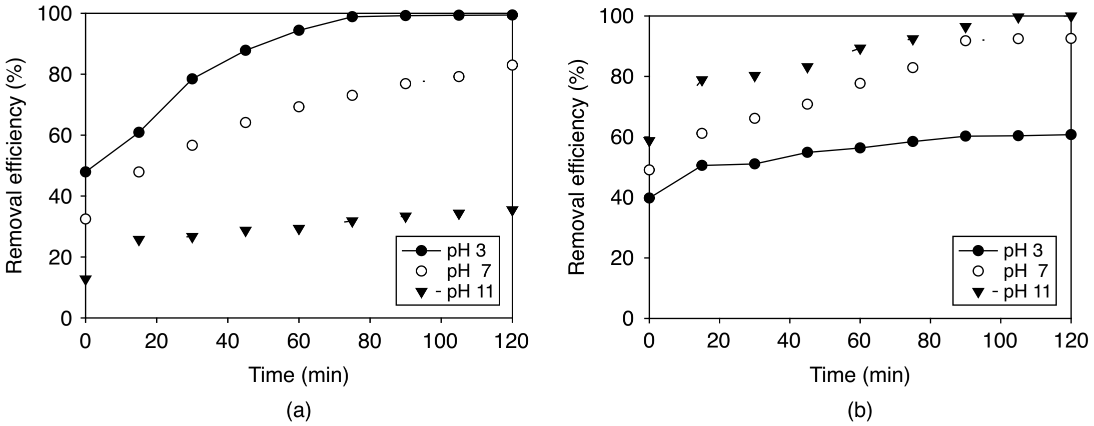


Fig. 4. Effect of solution pH on the removal of (a) Cr(VI) and (b) Ni(II) with UV/TiO$_2$ ([Cr(VI)] and [Ni(II)] = 15 mg l^{-1}, TiO$_2$ dosage = 1 g l^{-1}).

The redox potential of the electron in the conduction band of TiO$_2$ (E_{CB}) depends on the crystal form of TiO$_2$ and on the solution pH. In case of anatase, E_{CB} varies from ca. –0.06 V to ca. –0.86 V at pH 11.16. Considering a Nernstian dependence of E_{CB} on solution pH at a rate of –0.059 V/pH, TiO$_2$ has sufficient reducing power to cause nickel deposition. The band gap of TiO$_2$ is around 3.2 eV with energy of conduction band –0.3 eV and valence band +2.9 eV at pH 5.6. Therefore, any metal ions having a reduction potential less negative than –0.3 eV would potentially be reduced by photogenerated electrons [32]. Considering the photocatalytic reduction of Cu^{2+} reported by Reiche et al. [33], photocatalytic reduction of Ni^{2+} can be possible through the following mechanisms.

$$2[\mathrm{TiO_2} + h\nu \rightarrow \mathrm{e^-} + \mathrm{h^+}] \tag{2}$$

$$\mathrm{Ni^{2+}} + 2\mathrm{e^-} \rightarrow \mathrm{Ni^0} \tag{3}$$

$$\mathrm{H_2O} + 2\mathrm{h^+} \rightarrow 1/2\mathrm{O_2} + 2\mathrm{H^+} \tag{4}$$

$$\mathrm{Ni^{2+}} + \mathrm{H_2O} + h\nu \rightarrow \mathrm{Ni^0} + 1/2\mathrm{O_2} + 2\mathrm{H^+} \tag{5}$$

Lin and Rajeshwar reported the formation of nickel deposition on TiO$_2$ using X-ray photoelectron spectroscopy (XPS) after photocatalytic reaction [34].

Fig. 4a shows removal pattern of Cr(VI) at different solution pH. As the solution pH increased, removal of Cr(VI) decreased because of the different speciation of Cr(VI) and redox potential at different solution pH [18,27,31].

Under acidic condition:

$$\mathrm{Cr_2O_7^{2-}} + 14\mathrm{H^+} + 6\mathrm{e^-} \rightarrow 2\mathrm{Cr^{3+}} + 7\mathrm{H_2O} \qquad E^0 = 0.98\ \mathrm{eV\,(SHE)} \tag{6}$$

Under neutral condition:

$$\mathrm{CrO_4^{2-}} + 8\mathrm{H^+} + 3\mathrm{e^-} \rightarrow \mathrm{Cr^{3+}} + 4\mathrm{H_2O} \qquad E^0 = 0.56\ \mathrm{eV\,(SHE)} \tag{7}$$

Under basic condition:

$$\mathrm{CrO_4^{2-}} + 4\mathrm{H_2O} + 3\mathrm{e^-} \rightarrow \mathrm{Cr(OH)_3} + 5\mathrm{OH^-} \qquad E^0 = 0.24\ \mathrm{eV\,(SHE)} \tag{8}$$

Another reason for the decreased removal rate at higher pH may be attributed to the deposition of Cr(OH)$_3$ on the surface of TiO$_2$ [18]. This mechanism can be explained by the adsorption of Cr(VI) onto the surface of TiO$_2$ and subsequent redox reaction on the surface of TiO$_2$ as expressed in the below equations. Photocatalytic reduction of Cr(VI) is possible by directly capturing photo-generated electrons (Eq. (13)) as well as by indirectly getting electron from surface Ti^{3+} of TiO$_2$ (Eq. (12)). The original sources of electrons came from Eq. (10). The speciation of Cr^{3+} depends on the solution pH and hydrolyzed Cr(OH)$_3$ is favorable at high solution pH [18,31].

$$\mathrm{Cr^{6+}}_{\mathrm{suspension}} \rightarrow \mathrm{Cr^{6+}}_{\mathrm{adsorbed}} \tag{9}$$

$$3[\mathrm{TiO_2} + h\nu \rightarrow \mathrm{e^-} + \mathrm{h^+}] \tag{10}$$

$$3\left[\mathrm{Ti^{4+}} + \mathrm{e^-} \rightarrow \mathrm{Ti^{3+}}\right] \tag{11}$$

$$3\mathrm{Ti^{3+}} + \mathrm{Cr^{6+}}_{\mathrm{adsorbed}} \rightarrow \mathrm{Cr^{3+}}_{\mathrm{adsorbed}} + 3\mathrm{Ti^{4+}} \tag{12}$$

$$\mathrm{Cr^{6+}}_{\mathrm{adsorbed}} + 3\mathrm{e^-} \rightarrow \mathrm{Cr^{3+}}_{\mathrm{adsorbed}} \tag{13}$$

For UV irradiated TiO$_2$, there are two kind of Ti^{3+} produced: inner Ti^{3+} and surface Ti^{3+}. The inner Ti^{3+}

usually acts as recombination center which is detrimental to photocatalytic activity. On the other hand the surface Ti^{3+} is known as reactive center for photocatalytic process [18,31].

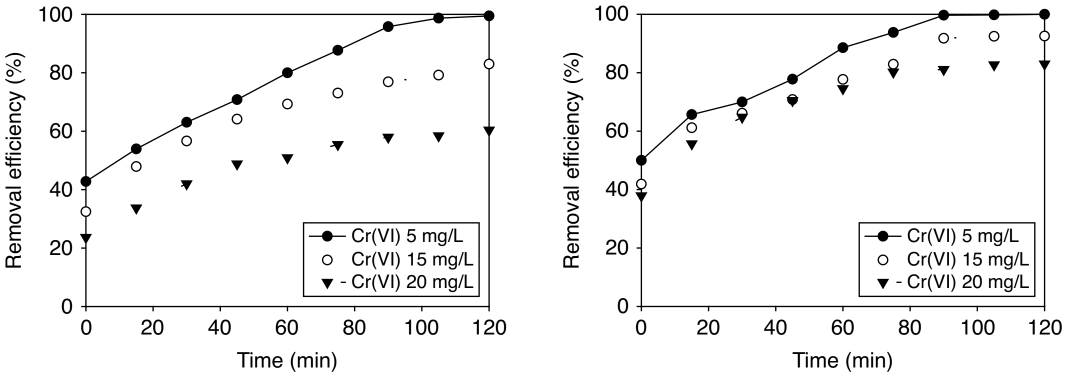
Fig. 4b shows removal pattern of Ni(II) at different solution pH. As the solution pH increased, removal of Ni(II) increased because of the favorable adsorption of Ni(II) onto the TiO_2 surface as well as the formation of reduced Ni(0) through photocatalytic reduction and more precipitation of Ni(II) as $Ni(OH)_2$ [9]. It is generally known that adsorption of cationic type heavy metal ion onto metal(hydr-)oxides is favorable at high pH because more negative surface charge developed on the surface of meta(hydr-)oxides and interaction between cationic metal ion and meta(hydr-)oxides increased [35].

3.3. Effect of Cr(VI) and Ni(II) concentration on the removal of Cr(VI) and Ni(II)

Removal of Cr(VI) and Ni(II) by UV/TiO_2 was investigated by varying the initial Cr(VI) and Ni(II) concentration (5, 15, 20 mg l^{-1}) at pH 7 and at constant TiO_2 dosage(1 g l^{-1}) for different time intervals. Fig. 5a and b show the effect of initial Cr(VI) and Ni(II) concentration on photocatalytic reduction efficiencies of Cr(VI) and Ni(II), respectively. It can be seen that removal efficiency of Cr(VI) and Ni(II) decreased as initial Cr(VI) and Ni(II) concentration increased. The presumed reason is that when the initial Cr(VI) and Ni(II) concentration increased, more Cr(VI) and Ni(II) molecules are reduced on the surface of TiO_2. Therefore the large amount of reduced species from Cr(VI) and Ni(II) is thought to have an inhibitive effect on further reduction of Cr(VI) and Ni(II) by electrons in the conduction band [8,10,17,27,36–41]. Because the initial concentration of Cr(VI) and Ni(II) employed in this study was low, the removal kinetics can be described adequately by a simplified first-order rate equation (Eq. (1)) [42,43]. First-order rate constants of both Cr(VI) and Ni(II) at three different concentrations are summarized in Table 1.

3.4. Effect of Cr(VI) on the removal of Ni(II) and vice versa

Simultaneous removal of Cr(VI) and Ni(II) by UV/TiO_2 was investigated at initial pH 7 and at constant catalyst dosage(1 g l^{-1}) for different time intervals. Fig. 6a and b show effect of initial Cr(VI) and Ni(II) concentration on the photocatalytic removal efficiencies of Cr(VI) and Ni(II), respectively. It can be seen that removal efficiency of Cr(VI) decreased in the presence of Ni(II) over the entire reaction time and vice versa. The presumed reason is that when both Cr(VI) and Ni(II) presents, competitive adsorption between Cr(VI) and Ni(II) on the surface of TiO_2 as well as competitive reduction between Cr(VI) and Ni(II) by electrons from conduction band of the TiO_2 might occur.

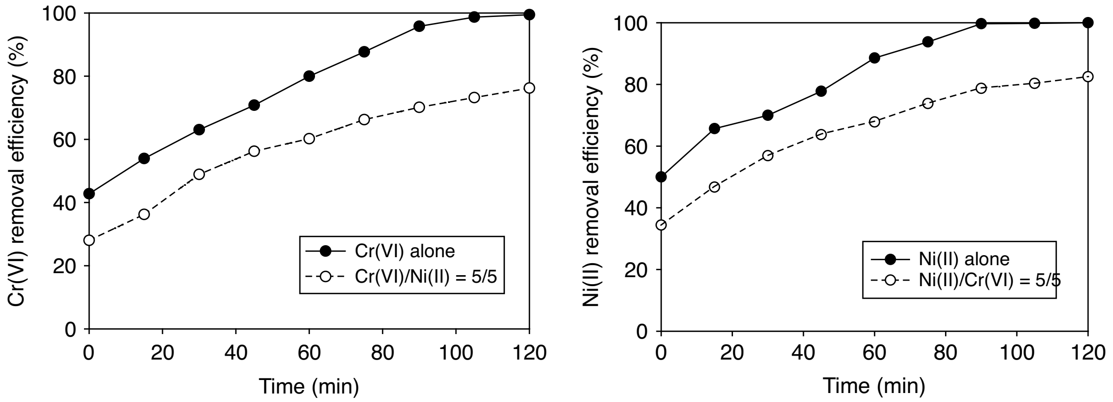


(a) Cr(VI) (b) Ni(II)

Fig. 5. Effect of initial Cr(VI) and Ni(II) concentrations on the removal of (a) Cr(VI) and (b) Ni(II) with UV/TiO_2 (pH = 7, catalyst dosage = 1 g l^{-1}).

Table 1
Experimental results for the photoreduction of Cr(VI) and Ni(II) onto TiO_2 in aqueous solution

pH	$[Cr(VI)]_0$(mg l^{-1})	k_1(min^{-1})	R^2	$[Ni(II)]_0$ (mg l^{-1})	k_1(min^{-1})	R^2
7	5	0.013	0.997	5	0.013	0.982
7	15	0.010	0.994	15	0.013	0.981
7	20	0.004	0.956	20	0.009	0.959



(a) Cr(VI) removal with and without presence of Ni(II)

(b) Ni(II) removal with and without presence of Cr(VI)

Fig. 6. Effect of Cr(VI) on the removal of Ni(II) and vice versa (pH = 7, catalyst dosage = 1 g l^{-1}). (a) Cr(VI) removal with and without presence of Ni(II) and (b) Ni(II) removal with and without presence of Cr(VI).

4. Conclusions

The major findings of this study are as follow:

1. Photocatalytic removal of Cr(VI) and Ni(II) increased with increasing the TiO_2 dosage because of the increased adsorption sites on the TiO_2 as well as the more generation of free electrons in the conduction band.
2. Photocatalytic reduction of Cr(VI) increased by decreasing pH because of the different speciation of Cr(VI) and redox potential at different solution pH. Another reason for the decreasing removal rate at higher pH may be increased deposition of $Cr(OH)_3$, which was produced from Cr(VI) reduction, on the surface of TiO_2. Also, as the solution pH increased, removal of Ni(II) increased because of the favorable adsorption of Ni(II) onto the TiO_2 surface as well as the formation of reduced Ni(0) through photocatalytic reduction and precipitated $Ni(OH)_2$ above neutral pH.
3. Removal efficiency of Cr(VI) and Ni(II) decreased as initial Cr(VI) and Ni(II) concentration increased. The presumed reason is that when the initial Cr(VI) and Ni(II) concentration increased, more Cr(VI) and Ni(II) molecules are reduced on the surface of TiO_2.
4. Photocatalytic reaction with illuminated TiO_2 can be used to reduce toxicity of heavy metal ions such as Cr(VI) and Ni(II) through reduction process from wastewater.

Acknowledgements

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